Model Bulk Mo-V-Te-O Oxide Catalysts for Selective Oxidation of Propane to Acrylic Acid

Jamal N. Al-Saeedi,[1] Vijay K. Vasudevan,[1,2] and Vadim Guliants[1]

[1]University of Cincinnati, Department of Chemical and Materials Engineering, Cincinnati, OH 45221-0012

[2]Argonne National Laboratory, Materials Science Division, Argonne, IL 60439

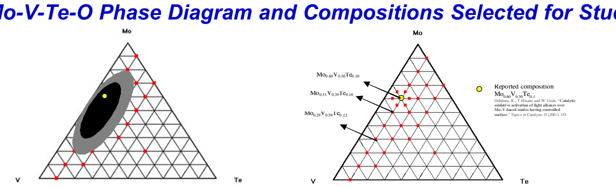
Scientific Achievement

- Model Mo-V-Te-O oxide catalysts were prepared by hydrothermal synthesis and characterized by x-ray diffraction, ICP and transmission electron microscopy.
- The crystal structures of the M1 and M2 phases proposed as active and selective in propane oxidation to acrylic acid over the bulk mixed Mo-V-Te-O catalysts were investigated.
- The crystal structure of M1 is hexagonal with space group *P6mm*, lattice parameters a = 7.1 Å, c = 4.05 Å and composition $Mo_{1.79}V_{1.85}Te_{0.1}O_{11.36}$ (Mo/V~1).
- The crystal structure of M2 is orthorhombic with space group *Pbca*, lattice parameters a = 21.25 Å, b = 27.14 Å, c = 4.03 Å and composition $Mo_{0.64}V_{0.32}Te_{0.1}O_{3.05}$ (Mo/V~2).
- The M2 phase was dominant in the Mo-V-Te-O catalyst. HRTEM observations revealed a unique pore structure in this phase, which has important implications for catalysis.
- The present results on the structure of M1 and M2 are in general agreement with previous reports, except for the space group of the M2 phase (*Pbca* vs. *Pba2*).
- The results obtained indicated that the bulk Mo-V-Te oxides represent a well-defined model catalytic system for fundamental studies of the surface molecular structure-activity/selectivity relationships in propane oxidation to acrylic acid.

Significance

- Selective propane oxidation to acrylic acid (AA) is:
  - ✓ Attractive due to abundance of low cost alkanes
  - ✓ Conversion to highly demanded olefins (propene) and oxygenate possible
  - ✓ Environmentally favored process
- Mixed metal Mo-V-Te-(Nb)-O oxide catalysts are particularly promising for the selective oxidation of propane to acrylic acid [1,2].
- These contain M1 and M2 phases proposed as active and selective phases [1,2].
- Tentative structural models for M1 and M2 have been proposed [3-5], but the detailed structures of these phases and the phase diagram have not been established.
- We have discovered that structurally similar and compositionally simpler three-component Mo-V-Te-O oxides containing the M1 and M2 phases are highly selective in propane oxidation [6].
- In the present study, we have determined that the structure and lattice parameters of M1 and M2 are similar to those reported by others [6], but the space group of M2 was determined to be different (*Pbca* vs. *Pba2*).

Mo-V-Te-O Phase Diagram and Compositions Selected for Study



Shaded Dark Region contains both M1 and M2 phases; Gray Region contains either M1 or M2 phases along with other impurity phases. The position of $Mo_{0.60}V_{0.30}Te_{0.10}$ is shown as a circle. Studied compositions are marked by red squares. Selected compositions that contain both M1 and M2 phases are shown with black arrows.

References

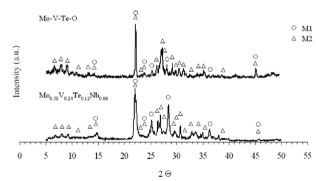
1. H. Watanabe and Y. Koyasu, *Appl. Catal.*, **194**, 479 (2000); M. Lin, M., *Appl. Catal.*, **207**, 1 (2001)
2. W. Ueda, W., N. F. Chen and K. Oshihara, *Chem.Comm.*, 517 (1999); *Top. in Catal.*, **15**, 153 (2001).
3. M. Aouine, J.M.M. Millet, J.L. Dubois, *Chem. Comm.*, **13**, 1180 (2001).
4. J.M.M. Millet, H. Roussel, A. Pigamo, J.L. Dubois, J.C. Jumas, *Appl. Catal. A*, **232**, 77 (2002).
5. D.J. Buttrey, P. DeSanto, Jr., R.K. Grasselli, Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002, PETR-031
6. J.N. Al-Saeedi, V.V. Guliants, V. K. Vasudevan, Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003, INOR-253; Communicated to *Catal. Comm.*

Hydrothermal Synthesis of Mo-V-Te-O Oxide Catalysts

- Reagents: Ammonium heptamolybdate (source of M^{6+}); $VOSO_4$ (source of V^{4+}); TeO_2 (source of Te^{4+})

Precursors Mixing → Hydrothermal Synthesis (72h at 175°C) → Filtration (Black Powder) → Calcination (Air/N_2)

X-Ray Diffraction Identifying M1 and M2 Phases in Mo-V-Te-O Catalysts



Lattice Parameters of M1 (Hexagonal, P6mm) and M2 (Orthorhombic, Pbca)

Mixed Metal Oxide	M1		M2		
	a, Å	c, Å	a, Å	b, Å	c, Å
Mo-V-Te-O [This work]	7.10	4.05	21.25	27.14	4.03
Mo-V-Te-Nb-O [3]	28.70	4.03	21.21	26.83	8.05
Mo-V-Te-Nb-O [5]	7.29	4.02	21.12	26.62	4.01

Composition of M1 from TEM-EDS

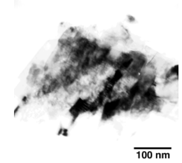
Synthesis Composition (ICP)	M1 phase composition	Mo	V
$Mo_{0.60}V_{0.30}Te_{0.10}O_x$	$Mo_{7.27}V_{9.08}Te_{1.00}O_{25.42}$	17.0	21.2
$Mo_{0.51}V_{0.39}Te_{0.10}O_x$	$Mo_{3.17}V_{4.69}Te_{1.00}O_{43.69}$	6.0	8.9
$Mo_{0.29}V_{0.59}Te_{0.12}O_x$	$Mo_{17.87}V_{18.53}Te_{1.00}O_{113.57}$	11.8	12.3

Composition of M2 from TEM-EDS

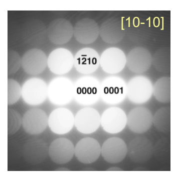
Synthesis Composition (ICP)	M2 phase composition	Mo	V	Te	O	Mo/V
$Mo_{0.60}V_{0.30}Te_{0.10}O_x$	$Mo_{9.08}V_{4.79}Te_{1.00}O_{24.04}$	23.3	12.3	2.6	61.8	1.89
$Mo_{0.51}V_{0.39}Te_{0.10}O_x$	$Mo_{2.20}V_{1.37}Te_{1.00}O_{19.30}$	9.2	5.8	4.2	80.8	1.60
$Mo_{0.29}V_{0.59}Te_{0.12}O_x$	$Mo_{6.41}V_{3.19}Te_{1.00}O_{30.51}$	15.6	7.7	2.4	74.2	2.01

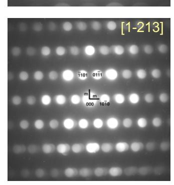
Structure and Morphology of M1 Phase

Hexagonal; P6mm; a=7.1A, c= 4.05Å

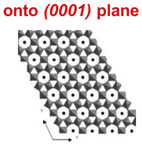


Misoriented Platelets of Nanoscale Dimensions



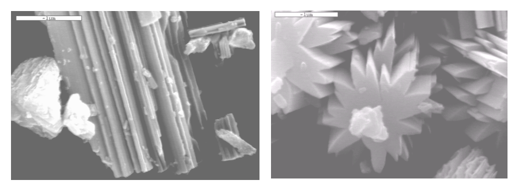


Projection of M1 structure onto *(0001)* plane



SEM Showing Morphology of Mo-V-Te-O Oxides

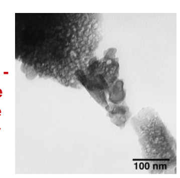
$Mo_6V_3Te_1O$ $Mo_3V_6Te_1O$

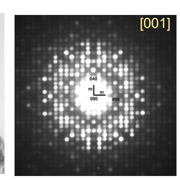


Structure and Morphology of M2 Phase

Orthorhombic; Pbca; a = 21.25Å, b =27.14Å, c = 4.03Å

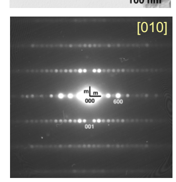
Mottled Structure - Evidence for some Disorder

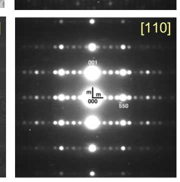




Glide planes Normal to a, b-axes

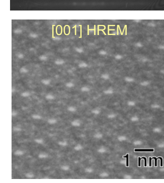
Glide plane/ Screw Axis Normal/ Parallel to c-axes

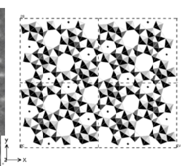




(001) Spots Appear due to Double Diffraction

Unique Pore Structure





Projection of M2 structure onto (001) plane

Acknowledgement

This work was supported by NSF, Career Award - CTS-0238962 (VG) and the Public Authority for Applied Education, Kuwait (JNS). The electron microscopy was performed using the facilities at the Argonne National Laboratory, MSD, Electron Microscopy Center

BES - DOE

MSD - ANL